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Perfluorinated rare earth metals catalyzed nitration of aromatic compounds

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Abstract

The nitration of aromatic compounds can be carried out in the presence of perfluorinated rare earth metal catalyst without halogenated organic solvent. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nitration; Aromatic compounds; Perfluorinated rare earth metal catalyst

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1. Introduction

Nitration of organic compounds has long been a very active and rewarding area of research and is the subject of a large body of literature. Extensive and well documented reviews have been published by Ingold [1], Olah [2,3,6], Schofield [4,5], and Ione [7], among others. Nitrations in manufacturing process require the use of potent mixtures of concentrated or fuming nitric acid with sulfuric acid leading to excessive acid waste streams and added expense. The obvious disadvantages of the commercial manufacturing process currently used has led to a substantial effort to develop viable alternatives, inter alia using solid acid catalysts, other sources of NO_2^+, organic nitrating agents, other acids replacing sulfuric acid, etc. Recently, it was found that Lanthanide(III) triflates (1–10 mol%) can catalyze the nitration of a range of simple aromatic compounds in good to excellent yield using stoichiometric quantities of 69% nitric acid and the only by-product is water and the catalyst (Scheme 1) can be readily recycled by simple evaporation [8]. However, these nitrations were carried out in 1,2-dichloroethane, an environmentally hazardous solvent, under refluxing. Herein, we wish to report a green nitration process using perfluorinated rare earth metals as catalysts without halogenated organic solvent.

2. Results and discussion

Kobayashi reported in 2000 that, $Sc(OSO_2C_8F_{17})_3$ $[Sc(OPf)_3]_3$ can be used as an efficient catalyst for the catalytic Diels–Alder or Aze Diels–Alder reaction [9]. Based on his results, we believe that such Lewis acids having perfluorinated long carbon chains can act as a phase transfer catalyst (PTC) as well for some other organic reactions. Thus, we attempted the nitration of aromatic compounds using $Ln(OSO_2C_8F_{17})_3$ as a catalyst and 60% HNO_3 as a nitric reagent without halogenated organic solvent (Scheme 2). Their results were summarized in Table 1. As can be seen from Table 1, without using halogenated organic solvent, the nitration of toluene indeed took place at 70 °C to give the nitrated toluene in good yield and the catalyst loading is only 0.05 mol% (Table 1, entry 1–4), although the yields are 50–60%. $Sc(OSO_2C_8F_{17})_3$ has the highest activity for catalytic nitration (entry 3), but it is also the most expensive rare earth metal. The orientation of this nitration has been also elucidated in Table 1. Various $Ln(OSO_2C_8F_{17})_3$ in general gave the similar orientation. Therefore, we selected $Yb(C_8F_{17}SO_3)_3$ as a general Lewis acid catalyst for nitration. From Table 1, when the catalyst loading reduce to 0.02 mol%, the nitration can still efficiently take place to give the nitrated product in good yields and $Yb(C_8F_{17}SO_3)_3$ is more effective than $Yb(OTf)_3$ for nitration of toluene under the same conditions (Scheme 2, Table 1, entry 5–6).

By means of the optimized reaction conditions, we next examined the nitration of other aromatic compounds (Scheme 3). The results were summarized in Table 2. The

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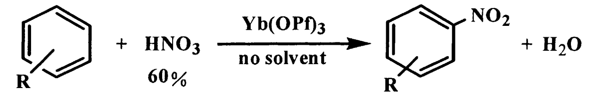
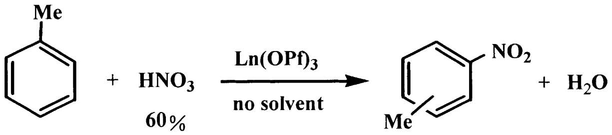


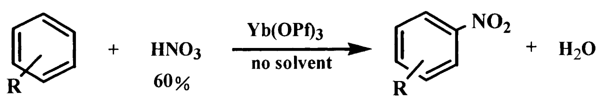
$Yb(OPf)_3$: $Yb(C_8F_{17}SO_3)_3$.

Scheme 1.



$Ln(OPf)_3$: $Ln(C_8F_{17}SO_3)_3$.

Scheme 2.



$Yb(OPf)_3$: $Yb(C_8F_{17}SO_3)_3$.

Scheme 3.

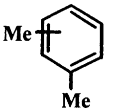
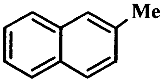
Table 1
Nitration of toluene using perfluorinated rare earth metals

Entry	$Ln(OPf)_3$	Catalyst (mol%)	Yield[a] (%)
1	$Yb(OPf)_3$	0.05	63[b]
2	$Eu(OPf)_3$	0.05	60
3	$Sc(OPf)_3$	0.05	65
4	$La(OPf)_3$	0.05	50
5	$Yb(OPf)_3$	0.02	60
6	$Yb(OPf)_3$	0.02	17

[a] Isolated yields.

[b] *p*:*m*:*o* = 45:1:54 (determined by GC).

Table 2
Nitration of various aromatic compounds using perfluorinated rare earth metals

R	Catalyst (mol%)	Yield[a] (%)
F	0.02	53[b]
Br	0.02	54[c]
H	0.02	30
Ph	0.02	32
	0.02	50
	0.02	60

[a] Isolated yields.

[b] *p*:*m*:*o* = 76:0:24 (determined by GC).

[c] *p*:*m*:*o* = 63:0:37 (determined by GC).

yields of the nitration products in general can reach 50–60% under 0.02 mol% catalyst loading.

In conclusion, we have discovered a very efficient nitration process in the presence of perfluorinated rare earth metal catalysts under mild reaction conditions. This new nitration process employs 0.02 mol% of perfluorinated rare earth metal as catalysts without using halogenated organic solvent. Thus, it is much eco-safer protocol of nitration. Efforts are underway to elucidate the more mechanistic details of this reaction and to identify systems enabling the other aromatic compounds, and the subsequent transformations, thereoff.

3. Experimental section

3.1. General

MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Mass spectra were recorded with a HP-5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. The orientation of nitration was determined by GC analysis. Flash column chromatography was carried out using 200–300 mesh silica gel. Isocyanates were purchased from Aldrich Co. $Ln(C_8F_{17}SO_3)_3$ was prepared from the reaction of $C_8F_{17}SO_3H$ with Ln_2O_3 according to the literatures [7].

3.2. General Procedure for the perfluorinated rare earth metals catalyzed nitration of aromatic compounds

To a solution of toluene (0.4 ml, 5.0 mmol) and 60% nitric acid (0.25 mg, 2.5 mmol) was added $Yb(C_8F_{17}SO_3)_3$ (2.1 mg, 0.05 mmol) and reaction mixture was stirred at 70 °C for 48 h. The reaction mixture was washed with water (10 ml) and extracted with dichloromethane (CH_2Cl_2). The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc =10/1) to give nitrotoluene as a yellow liquid. An amount of 215 mg, 63%; 2-nitrotoluene: ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.61 (3H, s, CH_3), 7.20–7.45 (2H, m, Ar), 7.48 (1H, d, $J = 7.5$ Hz, Ar), 7.96 (1H, d, $J = 7.5$ Hz, Ar); 3-nitrotoluene: ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.48 (3H, s, CH_3), 7.40–7.51 (2H, m, Ar), 7.92–8.09 (2H, m, Ar); 4-nitrotoluene: ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.48 (3H, s, CH_3), 7.33 (2H, d, $J = 8.4$ Hz, Ar), 8.13 (2H, d, $J = 8.4$ Hz, Ar). MS (EI) *m/z* 137 (M^+) [Calc. for $C_7H_8NO_2$ (137.1360): requires *M*, 137.0477. Found: M^+ 137.0464].

3.3. Nitration of p-fluorobenzene

A yellow oil, 194 mg, 55%; 4-nitrochlorobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.62 (2H, d, $J =$ 8.2 Hz, Ar), 8.06 (2H, d, $J = 8.2$ Hz, Ar); 2-nitrochlorobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.30–7.36 (3H, m, Ar), 7.75 (1H, d, $J = 7.8$ Hz, Ar). MS (EI) *m/z* 141 (M^+) [Calc. for $C_6H_5FNO_2$ (141.0999): requires M, 141.0226. Found: M^+ 156.9915].

3.4. Nitration of p-bromobenzene

A yellow solid, mp 96–110 °C, 278 mg, 55%; 4-nitrobromobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.59 (2H, d, $J = 8.5$ Hz, Ar), 8.0 (2H, d, $J = 8.5$ Hz, Ar); 2-nitrobromobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.27–7.33 (3H, m, Ar), 7.70 (1H, d, $J = 7.8$ Hz, Ar). MS (EI) *m/z* 202 (M^+) [Calc. for $C_6H_5BrNO_2$ (202.0055): requires M, 200.9425. Found: M^+ 200.9410].

3.5. Nitration of benzene

A yellow oil, 100 mg, 32%, ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.71 (2H, t, $J = 7.7$ Hz, Ar), 7.52–7.58 (1H, m, Ar), 8.24 (2H, d, $J = 7.8$ Hz, Ar); MS (EI) *m/z* 123 (M^+) [Calc. for $C_6H_5NO_2$ (123.1094): requires M, 123.0320. Found: M^+ 123.0333].

3.6. Nitration of biphenyl

A yellow solid, 150 mg, 30%, mp 45–50 °C, ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.27–8.28 (9H, m, Ar); MS (EI) *m/z* 199 (M^+) [Calc. for $C_{12}H_9NO_2$ (199.2054): requires M, 199.0633. Found: M^+ 199.0630].

3.7. Nitration of xylene

A yellow oil, 190 mg, 50%; 1,2-dimethyl-4-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.38 (6H, s, CH_3), 7.25 (1H, d, $J = 8.0$ Hz, Ar), 7.94–8.0 (2H, m, Ar); 1,3-dimethyl-5-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.42 (6H, s, CH_3), 7.30 (1H, s, Ar), 7.83 (2H, s, Ar); 1,4-dimethyl-2-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (3H, s, CH_3), 2.55 (3H, s, CH_3), 7.20–7.33 (2H, m, Ar), 7.78 (1H, s, Ar); 2,3-dimethyl-1-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.37 (6H, s, CH_3), 7.08–7.45 (2H, m, Ar), 7.58 (1H, d, $J = 7.8$ Hz, Ar); 2,4-dimethyl-1-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.40 (3H, s, CH_3), 2.60 (3H, s, CH_3), 7.11–7.16 (2H, m, Ar), 7.92 (1H, d, $J = 7.9$ Hz, Ar); 2,6-dimethyl-1-nitrobenzene: ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.30 (6H, s, CH_3), 7.11–7.28 (3H, m, Ar). MS (EI) *m/z* 151 (M^+) [Calc. for $C_8H_9NO_2$ (151.1626): requires M, 151.0633. Found: M^+ 151.0630].

3.8. Nitration of 2-methylnaphthalene

A yellow solid, mp 38–42 °C, 283 mg, 60%; a mixture of isomer. MS (EI) *m/z* 187 (M^+) [Calc. for $C_{11}H_9NO_2$ (187.1947): requires M, 187.0633. Found: M^+ 187.0625].

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